PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-348343
(43)Date of publication of application : 04.12.2002

(51)Int.Cl. C08F297/06
C08F 4/606
C08L101/00
//(C08L101/00
C08L 53:00)

(21)Application number : 2001-159028
(22)Date of filing : 28.05.2001

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(54) OLEFIN POLYMER, ITS MANUFACTURING METHOD AND THERMOPLASTIC RESIN COMPOSITION COMPRISING THE POLYMER

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an olefin polymer useful for a polyolefin composite material field and a manufacturing field of a compatibilizer to easily make a design of a composite material.
SOLUTION: The olefin polymer comprises block bonding a polymer chain (I) comprising at least one monomer selected from among ethylene, a 3-20C α-olefin, a cyclic olefin, styrene and its derivatives, and still another polymer chain (II) comprising at least one monomer selected from among the ethylene, the 3-20C α-olefin, the cyclic olefin, the styrene, and its derivatives, the polymer chain (I) differing from the polymer chain (II) in at least one among a kind of the monomer, stereoregularity, and a copolymerization composition [but, except when only the styrene exists in both the polymer chain (I) and the polymer chain (II)], and having a graft structure based on a macromonomer.

LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]
[Date of final disposal for application]
[Patent number]
[Date of registration]
[Number of appeal against examiner's decision of rejection]
[Date of requesting appeal against examiner's decision of rejection]
[Date of extinction of right]

* NOTICES *

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CLAIMS

[Claim(s)]
[Claim 1] The polymer chain which consists of the monomer more than a kind chosen from ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative [I], It consists of the monomer more than a kind chosen from ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative. Block association of the polymer chain [II] for which one or more of a monomer kind, stereoregularity, and copolymerization presentations differ from a polymer chain [I] is carried out (however, the case where only styrene exists in both a polymer chain [I] and a polymer chain [II] is removed.). And an olefin system polymer with the graft structure based on a macro monomer [I].
[Claim 2] The alpha olefin independence of carbon numbers 3-20, or the alpha olefin of carbon numbers 3-20 (a), Ethylene, the alpha olefin of carbon numbers 3-20 (b) (however, an alpha olefin (b) differs from an alpha olefin (a)), The polymer chain which consists of the monomer more than a kind chosen from an annular olefin, styrene, and its derivative [I], It consists of the monomer more than a kind chosen from ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative. Block association of the polymer chain [II] for which one or more of a monomer kind, stereoregularity, and copolymerization presentations differ from a polymer chain [I] is carried out. The olefin system polymer which has the stereoregularity of a polymer chain [I] in 35 - 100% of range with a meso pentad molar fraction [mmmm] or a raceme pentad molar fraction [rrrr] [II].
[Claim 3] The polymer chain which consists of the monomer more than a kind chosen from ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative [I], It consists of the monomer more than a kind chosen from ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative. It has the polymer chain [II] for which one or more of a monomer kind, stereoregularity, and copolymerization presentations differ from a polymer chain [I], and is a solid-state. In the relaxation rate of the long duration relaxation component for which it asked by 1 H-NMR measurement The relaxation rate of a component is set to 0 (1 / R1) (unit: 1-/second) for a long time in the physical mixture which consists of a polymer chain [I] and a polymer chain [II]. the relaxation rate of the prolonged component of an olefin system polymer [III] -- ** (unit (1 / R1): 1-/second) -- the time of carrying out -- 0 (1 / R1) (1 / R1) The following formula (1)
[(1 / R1) /(1 / R1) 0] >=1.05 (1)
The olefin system polymer to satisfy [III].
[Claim 4] A polymer chain [I] An ethylene independent chain or ethylene, and the alpha olefin of carbon numbers 3-20, It is the ethylene copolymerization polymer chain which consists of the monomer more than a kind chosen from an annular olefin, styrene, and its derivative. It is the polymer chain to which a polymer chain [II] changes from the monomer more than a kind chosen from the alpha olefin and annular olefin of ethylene and carbon numbers 3-20. The olefin system polymer according to claim 1 to 3 which is an ethylene system polymer with which the ethylene content exceeds 40, and an olefin system polymer is less than [100 mol %], and uses ethylene as a principal component.
[Claim 5] A polymer chain [I] A propylene independent chain or a propylene, It is the propylene

copolymerization polymer chain which consists of the monomer more than a kind chosen from ethylene, the alpha olefin of carbon numbers 4-20, an annular olefin, styrene, and its derivative. A polymer chain [II] Ethylene, the alpha olefin of carbon numbers 3-20, It is the polymer chain which consists of the monomer more than a kind chosen from an annular olefin, styrene, and its derivative. The olefin system polymer according to claim 1 to 3 which is a propylene system polymer with which the propylene content exceeds 40, and an olefin system polymer is less than [100 mol %], and uses a propylene as a principal component.

[Claim 6] More than a kind of the alpha olefin of the alpha olefin polymer chain to which a polymer chain [I] changes from the monomer more than a kind chosen from the alpha olefin of carbon numbers 4-20, or carbon numbers 4-20 It is the alpha olefin copolymerization polymer chain which consists of the monomer more than a kind chosen from an annular olefin, styrene, and its derivative. A polymer chain [II] Ethylene, the alpha olefin of carbon numbers 3-20, It is the polymer chain which consists of the monomer more than a kind chosen from an annular olefin, styrene, and its derivative. The olefin system polymer according to claim 1 to 3 which is an alpha olefin system polymer with which the alpha olefin content of the carbon numbers 4-20 exceeds 40, and an olefin system polymer is less than [100 mol %], and uses an alpha olefin as a principal component.

[Claim 7] The metallic compounds chosen from the 3-10th groups of a periodic table, actinoid ones, and a lanthanoids are included as an indispensable component. The compound catalyst which consists of two or more sorts of catalysts from which at least one of the controllabilities of the stereoregularity and copolymerization to the monomer to be used differs is used. The manufacture approach of the olefin system polymer according to claim 1 to 6 characterized by carrying out the polymerization of two or more sorts of monomers chosen from ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative.

[Claim 8] One of the catalysts which form a compound catalyst is the following conditions (a).

(a) -- the polymerization engine performance to the monomer (Mg and description) of arbitration which is the catalyst which has the polymerization engine performance to a kind of monomer chosen from ** ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative, and is different from the ** above-mentioned **, and the polymerization engine performance to the monomer (Mh and description) of the above-mentioned ** -- the following type (2a) -- and (2b) --

0 <=[Mg] P/[Mg] F<=0.02 (2a)

0.5 <=[Mh] P/[Mh] F<=100 (2b)

However, [Mg] F : Monomer Mg A preparation presentation is expressed and it is Monomer Mg by total of the charge (unit: mol) of all monomers. Value P which broke the charge (unit: mol) [Mg] : A polymer presentation is expressed. Mg when setting to 1 total (the number of mols) of the monomer which constitutes a polymer The number F of monomers [Mh] : Monomer Mh A preparation presentation is expressed. It is Monomer Mh by total of the charge (unit: mol) of all monomers. Value P which broke the charge (unit: mol) [Mh] : Mh when setting to 1 total (the number of mols) of the monomer which expresses a polymer presentation and constitutes a polymer The manufacture approach according to claim 7 which is what satisfies the number of monomers.

[Claim 9] A compound catalyst is the following conditions (b).

(b) -- the copolymeric ability to monomers other than the above-mentioned ** which is the catalyst which has the polymerization engine performance to a kind of monomer chosen from ** ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative, and is chosen from ** ethylene, the alpha olefin of carbon numbers 3-20, an annular olefin, styrene, and its derivative -- two sorts of catalysts (Catalyst k and Catalyst l) -- setting -- the following type (3a) -- and (3b) --

1.2 <=[([Mi] / [Mj]) k]/[([Mi] / [Mj]) l] <=100 (3a)

([Mi] / [Mj]) k >=[([Mi] / [Mj]) l (3b)

However, [([Mi] / [Mj]) k]: Monomer Mi of the copolymer manufactured according to Catalyst k Monomer Mj Ratio of a content (unit: mol % / mol %)

[([Mi] / [Mj]) l]: Monomer Mi of the copolymer manufactured according to Catalyst l Monomer Mj

Ratio of a content (unit: mol % / mol %)
The manufacture approach according to claim 8 which is what is satisfied.
[Claim 10] (c) c [the following (c) and] Reach in copolymerization which consists more than of a kind chosen from a monomer, and the ethylene and the annular olefin more than a kind chosen from the polymerization of the monomer more than a kind chosen from the alpha olefin of carbon numbers 3-20, styrene, and its derivative and the alpha olefin of carbon numbers 3-20, styrene, and its derivative (e).
(c) The manufacture approach according to claim 8 using two or more sorts of catalysts as which AISO tacticity is chosen from the catalyst in which a polymerization is possible with a meso pentad molar fraction [mmmm] in the atactic polymer with which the catalyst (d) syndiotacticity in which a polymerization is possible corresponds the polymer of 35 - 100% of range with a raceme pentad molar fraction [rrrr] in the polymer of 35 - 100% of range to neither the catalyst (e) in which a polymerization is possible nor (c) nor and (d).
[Claim 11] The manufacture approach according to claim 8 that one of the catalysts which form a compound catalyst is the catalyst which generates an olefin system macro monomer [claim 12] The metallocene compound with which a catalyst has (1) cyclopentadienyl frame, (2) chelate compounds, and the (3) following general formula (G)
MR41a R42b R43c R44d (M shows the metallic element of the 4-8th groups of the periodic table, or the lanthanide series, R41, R42, R43, and R44 show the radical chosen from a halogen, a hydrocarbon group, halogenated hydrocarbon, and an alkoxy group, and even if R41, R42, R43, and R44 are the same, they may differ.) a, b, c, and d are the integers of 0-4. The manufacture approach according to claim 7 to 11 which is what consists of co-catalyst components more than a kind chosen from the metallic compounds chosen from the compound expressed, and (4) aluminoxane, the ionizing agent which reacts with (5) transition metals and generates an ionicity compound, (6) Lewis acid and the alkyl metallic compounds of the 1-3rd groups of (7) periodic tables.
[Claim 13] The thermoplastics constituent whose content of this olefin system polymer it consists of an olefin system polymer according to claim 1 to 6 and thermoplastics, and is 0.01 to 30 in constituent mass %.
[Claim 14] The thermoplastics constituent according to claim 15 which is that in which thermoplastics contains more than a kind of the monomer chain which constitutes an olefin system polymer according to claim 1 to 6.
[Claim 15] The constituent which consists of an olefin system polymer according to claim 1 to 6 and thermoplastics solid-state It carries out. the relaxation rate of the prolonged relaxation component of this constituent for which it asked by 1 H-NMR measurement -- ** (unit (1 / R1): 1-/second) -- When the relaxation rate of the prolonged relaxation component of the thermoplastics constituent which does not contain an olefin system polymer according to claim 1 to 8, or thermoplastics is set to 0 (1 / R1) (unit: 1-/second) (1 / R1) 0 (1 / R1) Thermoplastics constituent according to claim 16 or 17 with which are satisfied of the following type (4) [(1 / R1) /(1 / R1) 0] >=1.01 (4)
The thermoplastics constituent according to claim 13 or 14 to satisfy.
[Claim 16] The thermoplastics constituent according to claim 13 to 15 with which a constituent contains an additive.
[Claim 17] The Plastic solid acquired by carrying out melting shaping of the thermoplastics constituent according to claim 13 to 16.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the thermoplastics constituent which contains a useful olefin system polymer, its manufacture approach, and this polymer in the manufacture field of the compatibilizer which makes easy the design of the polyolefine system composite-material field and composite material.

[Translation done.]

PRIOR ART

[Description of the Prior Art] From the former, desired physical properties and a configuration are given by the shaping approaches that are chemically stable as for polyolefine, are excellent in weatherability, cannot be easily invaded by chemicals, and are excellent in a mechanical strength, and it is [object / various Plastic solids, for example a sheet, a film, an injection-molding object, a blow molding object, a foaming object a vacuum-forming object, / rotational casting] various, and it is used for various applications on a large scale. Moreover, the motion which mitigates an environmental load has been established from the rise of consciousness to the environmental protection of these days to plastics at large. Polyolefine system resin is excellent in recycle nature, shaping is easy, since it is hard to generate a harmful component by incineration, it is resin which agrees most in environmental load reduction, therefore the opportunity of a polyolefine system ingredient used further from now on increases, and it is presumed that demand characteristics are also developed. However, the various demands cannot be met in using one sort of polyolefine ingredients. Then, compound-izing some polyolefine ingredients from the former as a means for meeting this demand has been performed. However, generally, between polyolefines, since it was an immiscible system, control of mol follow G had a limit and there was a limitation in pulling out the description of each resin originally expected from the multicomputer system ingredient by compound.
[0003] As an example of the conventional propylene polymerization method, the propylene polymerization by the metallocene catalyst non-constructing a bridge is reported by "Exxon, Macromolecules 31, and 5343-5351 (1999)." In detail, if the polymerization of the propylene is carried out with the permutation indenyl complex of the mold non-constructing a bridge, for example, screw (2-phenyl indenyl) zirconium dichloride / MAO (methyl aluminoxane) catalyst, it is reported that the polypropylene of the multi-block type which consists of an isotactic chain and an atactic chain generates. Although [this report] the catalyst structure in a polymerization process changes and a block copolymer generates, unlike the block copolymer with common block ream chain length, rather than the so-called common block copolymer with that property it is short and long [block ream chain length], it has the property near a random copolymer. Therefore, when using as a phase vitrification component of a multicomputer system polymer, the engine performance about adhesion of a polymer interface required in order to control the physical properties of a multicomputer system, and control of the diameter of a particulate material by the surface activity effectiveness is low. Moreover, expanding the molecular weight distribution of an ethylene system polymer according to a compound catalyst is proposed by JP,60-35006,A,. JP,64-74202,A, and JP,3-203904,A. This is the technique of expanding molecular weight distribution in order to raise the moldability of metallocene catalyst system polyethylene. The polyethylene system resin manufactured using the so-called metallocene catalyst has narrow molecular weight distribution, the melting resin fluidity at the time of a fabricating operation is low, and productivity is low in film shaping, extrusion molding, etc., and many problems were held in the appearance of shaping stability and mold goods etc. In order to manufacture the polyethylene system resin with which molecular weight differs by the same polymerization reaction field as the technique of solving this problem, consequently to make molecular weight distribution expand, using two sorts of catalysts is proposed.

[0004] However, in these official reports, for the purpose of the technique about compound-izing of the polyolefine of an immiscible system, if, it does not break, and the concrete disclosure is not carried out, either. This is clear from description of the description in the above-mentioned official report. That is, as for each metallocene catalyst given in the above-mentioned open official report, the copolymeric one between olefins is high. Even if it sees a concrete operation gestalt, and the copolymerization presentation is similar with both catalyst and exchange reaction advances between catalytic activity point sites, the copolymer which can recognize the block structure is not generated substantially. Furthermore, it is related with the elastomer and constituent of polypropylene which consist of a different stereoregularity block. "J.Polym.Sci., PartA 37, No14, 2439-2445 (1999)", "Soc.Plast.Eng .Annu.Tech.Conf., 157th, No1, and 3978-3980 (1999" --) It is indicated by the U.S. Pat. No. 6124400 number and the U.S. Pat. No. 5756614 number, and the block copolymer is generated in these by the exchange reaction between catalyst growth sites. Here, it is indicated about the elastomer of the polymer alloy containing the ethylene / alpha olefin block copolymer, the PE-b-ethylene / alpha olefin block with which the SPS-b-APS, IPP-b-APP, IPP-b-SPP, IPP-b-APP, and PE-b-branching PE differs from presentation distribution, and PP system. However, when adding as a compatibilizer of polyolefine system composite material, in order to make the adhesive property of gestalt control or a polymer interface discover since the generation rate of the block object by site exchange is low, it does not have sufficient engine performance. Moreover, there is no publication of graft structure and it differs from this invention intrinsically.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] the compound compatibility in the thermoplastics constituent with which the olefin system polymer of this invention can control easily physical-properties manifestation factors, such as logy [MORUHO] and interface reinforcement, especially in the combination of an immiscible system -- it is suitable as a degassed part.

[Translation done.]

TECHNICAL PROBLEM

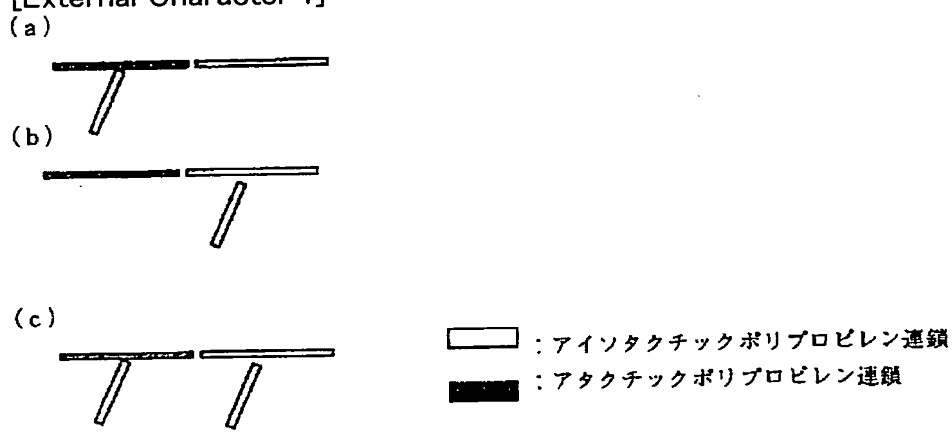
[Problem(s) to be Solved by the Invention] the compound compatibility in the thermoplastics constituent which this invention was made in view of the above-mentioned situation, and can control easily physical-properties manifestation factors, such as logy [MORUHO] and interface reinforcement, especially in the combination of an immiscible system -- it aims at offering an olefin system block graft copolymer and an olefin system polymer suitable as a degassed part.

[Translation done.]

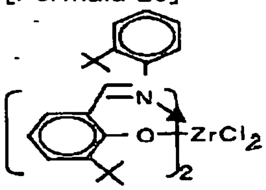
EXAMPLE

[Example] Next, although an example explains this invention to a detail further, this invention is not limited at all by these examples. in addition, the following -- setting -- LiPP -- in isotactic polypropylene and APP, atactic polypropylene and SPS mean syndiotactic polystyrene and PE means [low isotactic polypropylene and SPP / syndiotactic polypropylene and IPP] polyethylene.
[0141] 400ml [of dehydration toluene] and triisobutylaluminum 0.5 millimol was supplied to the proof-pressure autoclave made from stainless steel of an example 1 (manufacture of the block copolymer of LiPP and SPP), and 1.6l. of example of comparison 1(1) polymerization content volume, and it stirred at the room temperature for 10 minutes. 4.0 millimols (1.47 mols [l.] /, made in Albemarle, 14.5 % of the weight content of trimethylaluminums) of methyl aluminoxane were supplied to this, and temperature up was carried out to 45 degrees C. 0.4 micromole and three micromole of isopropylidene (cyclopentadienyl) (fluorenyl) dichloro zirconiums were supplied for zirconium dichloride (3(2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)-trimethylsilyl methylene-indenyl) to this. After the reaction termination which continued supplying so that a propylene may be introduced into an autoclave and it may become fixed with 0.8MPa(s) (gage pressure) with a partial pressure, controlled temperature at 50 degrees C, and performed the polymerization for 60 minutes, by depressuring, the unconverted gas was discharged, a small amount of methanol was added, and the reaction was suspended. After having thrown the reaction mixture into the 2l. methanol, depositing the copolymer and fully washing, the 120g block graft copolymer was obtained by filtration and desiccation (example 1).
(2) The assessment ** limiting viscosity [eta] of a block copolymer was measured in the 135-degree C decalin using the VMR[by RIGOSHA& Co., Ltd.]-053 mold automatic viscometer (also setting below the same). The limiting viscosity [eta] of a block copolymer was 2.5 deciliters/g.
** In order to show clearly that block copolymerization is carried out, extraction separation was carried out by the extraction separation method. That is, after stirring a block copolymer for 30 minutes, dissolving it with polymer concentration 2.5 mass % and the temperature of 50 degrees C by the heptane solvent system and carrying out solid liquid separation by filtration, extraction separation of the solid-state part was further carried out 4 times under these conditions. The heptane insoluble element finally separated by desiccation was obtained. This thing is equivalent to the syndiotactic polypropylene with which the intermingled low isotactic polypropylene was separated thoroughly. This was made into the assessment sample.
Moreover, in the above (1), the polymerization of the syndiotactic polypropylene was carried out without using zirconium dichloride (3(2 (1, 2'-dimethyl silylene), 1'-dimethyl silylene)-trimethylsilyl methylene-indenyl) (example 1 of a comparison). The sample was manufactured by the same actuation as the above using this, and it considered as the comparison sample. As a result of performing 13C-NMR analysis, the syndiotacticity [rrrr] of an assessment sample was 80.2%, and [rrrr] of a comparison sample was 86.6%. Moreover, the signal of the polypropylene which has the eye SOTAKU tacticity acquired by zirconium dichloride on the NMR chart (1, 2'-dimethyl silylene) (2, 1'-dimethyl silylene) of an assessment sample (3-trimethylsilyl methylene-indenyl) was observed. Therefore, if this copolymerization system is block copolymerization, it will be concluded.

[0142] Example 2 (manufacture of the block graft copolymer of IPP and SPP)
The metallocene system catalyst component used in the example 1 was changed as follows, and the block graft copolymer was manufactured. That is, the amount of the methyl aluminoxane used was made into 7 millimols, and hafnium dichloride 4 micromole and isopropylidene (cyclopentadienyl) (fluorenyl) dichloro zirconium 2 micromole were used as a transition-metals compound (indenyl) (1, 2'-dimethyl silylene) (2, 1'-dimethyl silylene). Consequently, the 92.5g block graft copolymer was obtained. The limiting viscosity [eta] of the block copolymer measured at decalin 135 degree C was 2.5 deciliters/g.
[0143] The metallocene system catalyst component used in the example 3 (manufacture of the block graft copolymer of IPP and APP) and the example of comparison 2(1) polymerization example 1 was changed as follows, and the block graft copolymer was manufactured. That is, the amount of the methyl aluminoxane used was made into 6 millimols, and two micromole and (1, 2'-dimethyl silylene) (2, 1'-dimethyl silylene) (indenyl) hafnium dichloride 4 micromole were used for Cp* TiCl (tBuN (SiMe2))2 (CGC catalyst) as a transition-metals compound. Consequently, the 85g block graft copolymer was obtained (example 3).
(2) The limiting viscosity [eta] of the block copolymer measured at assessment ** decalin 135 degree C of a block graft copolymer was 1.85 deciliters/g.
** In order to show clearly that block copolymerization is carried out, the heptane insoluble element was separated like assessment of an example 1 by the extraction separation method. This thing is equivalent to the isotactic polypropylene from which the intermingled atactic polypropylene was separated thoroughly. This was made into the assessment sample. Moreover, in the above (1), the polymerization of the isotactic polypropylene was carried out without using Cp* TiCl (tBuN (SiMe2))2 (CGC catalyst) (example 2 of a comparison). The sample was manufactured by the same actuation as the above using this, and it considered as the comparison sample. As a result of performing 13C-NMR analysis, the AISO tacticity [mmmm] of an assessment sample was 65.6%, and [mmmm] of a comparison sample was 80.6%. Moreover, the signal of the polypropylene of the atactic structure acquired by Cp* TiCl (tBuN (SiMe2))2 (CGC catalyst) was observed by the NMR chart of an assessment sample. Therefore, if this copolymerization system is block polymerization, it will be concluded. Furthermore, in order to show clearly that it has branching structure, the inertia square radius of the polymer of the dissolution condition over molecular weight was absolutely measured with GPC-light scattering measurement. As an assessment sample, the polymer of an example 2 was used as it was. Consequently, it checked that the value had long-chain branching, i.e., graft structure, clearly from 0.95 and a small thing as compared with g value of the polypropylene which does not include the usual branching. Moreover, if it takes into consideration that the exchange reaction of metal-polymer association advances among two sorts of catalysts, it can be said that the obtained copolymer is a block graft copolymer containing the following structure model chain (a), (b), and (c).
[0144]
[External Character 1]



[0145] Example 4 (manufacture of the block copolymer which consists of PE, and ethylene / propylene copolymerization chain)
As a chelate complex, it is [0146].
[Formula 23]



[0147] It came out and chelate complex A expressed was used. 800ml of dehydration toluene and 7.0 millimols (1.47 mols [l.] /, made in Albemarle, 14.5 % of the weight content of trimethylaluminums) of methyl aluminoxane were supplied to the proof-pressure autoclave made from stainless steel of 2l. of content volume, and temperature up was carried out to 45 degrees C. Four micromole and the three micromole above-mentioned chelate complex A were supplied for the isopropylidene (cyclopentadienyl) (fluorenyl) dichloro zirconium to this as a metallocene catalyst. Starting a 8 normal N liter / min for a propylene, starting supply for ethylene by 2 normal liters / min to this, and holding this flow rate, polymerization temperature was controlled so that 50 degrees C and the polymerization preassure force served as 0.7MPa(s) (gage pressure), and the copolymer was manufactured. Consequently, the 112g block graft copolymer was obtained. The limiting viscosity [eta] of the block copolymer measured at decalin 135 degree C was 1.8 deciliters/g.
[0148] Example 5 (manufacture of the block copolymer which consists of PE, and ethylene / propylene copolymerization chain)
The metallocene system catalyst component used in the example 4 was changed as follows, and the block graft copolymer was manufactured. That is, the amount of the methyl aluminoxane used was made into 7 millimols, and three micromole and (1, 2'-dimethyl silylene) (2, 1'-dimethyl silylene) (indenyl) hafnium dichloride 4 micromole were used for chelate complex A as a transition-metals compound. Consequently, the 92g block graft copolymer was obtained. The limiting viscosity [eta] of the block copolymer measured at decalin 135 degree C was 1.3 deciliters/g.
[0149] (Measurement of the relaxation velocity ratio by Pulse NMR)
** In the preparation examples 1-5 of a comparison sample, the polymer was manufactured among the metallocene compounds of two sorts of transition metal catalyst components only using one side, without changing other conditions. Thus, two sorts of polymers guided from each metallocene compound were obtained independently. In the manufacture process of this, i.e., a polymer, the polymerization gestalt which eliminated all the elementary process resulting from contact of two sorts of metallocene compounds is meant. The dryblend of the anti-oxidant BHT was carried out with 500 ppm, melting kneading of the polymer from which two sorts of these structures differ was carried out for 7 minutes with the lab PURASUTO mill made from an Oriental energy machine (60ml of content volume, rotational-speed 50rpm), and the constituent was produced. Kneading temperature was made into 220 degrees C. These kneading objects were collected, after cooling, it ground, and the constituent pellet was obtained. This was made into the comparison sample.
** The block copolymer or block graft copolymer manufactured in the preparation examples 1-5 of an assessment sample also carried out kneading grinding on the comparison sample said conditions with the lab plus mill made from an Oriental energy machine, and produced the pellet. [as well as the above]
** According to the measuring method shown in the assessment place, the long duration relaxation rate was measured from assessment of the solid-state NMR of this assessment sample and an example 1, and the relaxation velocity ratio to a comparison sample was measured. A relaxation velocity ratio is shown in the 2nd table.
[0150]

[A table 2]

第２表

	緩和速度比 [（1／R_1）／（1／R_1）$_0$]
実施例１	1．２２
実施例２	1．２５
実施例３	1．３１
実施例４	1．１８
実施例５	1．２２

[0151] Dissolution mixing was carried out on the conditions shown in the 3rd table, using BHT500ppm as 300ml of manufacture para xylene of the polyolefine constituent by examples 6-10 (manufacture of a polyolefine constituent) and the example 4 of a comparison - 6(1) solution blend, and an antioxidant. The amount of polymer dissolutions was set to 3-3.7g. The polymer mixed solution was thrown into the 3l. methanol 3 hours after, having checked to homogeneity that resin was dissolving and stirring to it, and reprecipitation recovered the polyolefine constituent. After carrying out a ** exception, reduced pressure drying was carried out at 80 degrees C, and it checked having grown into constant weight and considered as the polyolefine constituent (examples 12-14). Moreover, the polypropylene constituent was obtained like the above except not blending a block copolymer (examples 4-6 of a comparison).

(2) Solid-state Using the constituent manufactured by the measurement above (1) of 1 H-NMR, the plate was produced with a heat press, this was ground and the sample of a pellet type was produced. It measured by the approach shown previously using this sample. Measurement temperature was made into 90 degrees C. A measurement result is shown in the 3rd table.

[0152]

[A table 3]

第３表－１

		実施例６	比較例３	実施例７	比較例４	実施例８	比較例５
樹脂の組成（質量％）	HDPE (A)						
	LLDPE (B)						
	IPP (C)			８３	８３	８３	８３
	SPP (D)	８３	８３	１７	１７		
	APP (E)					１７	１７
	LiPP (F)	１７	１７				
ブロック共重合体（重量部）		実施例１ １０		実施例２ ５		実施例３ １０	
緩和速度（1/R_1）（1/秒）			－		－		－
緩和速度（1/R_1）$_0$（1/秒）		－		－		－	
緩和速度比 [（1/R_1）/（1/R_1）$_0$]			－		－		－
均一溶解性		○	○	○	○	○	○

[0153]

[A table 4]

第3表－2

		実施例9	比較例6	実施例10	比較例7
樹脂の組成（質量%）	HDPE (A)	17	17	17	17
	LLDPE (B)				
	IPP (C)			83	83
	SPP (D)	83	83		
	APP (E)				
	LiPP (F)				
ブロック共重合体（重量部）		実施例4 10		実施例5 5	
緩和速度 $(1/R_1)$ (1/秒)			−		−
緩和速度 $(1/R_1)_0$ (1/秒)		−		−	
緩和速度比 $[(1/R_1)/(1/R_1)_0]$			−		−
均一溶解性		○	○	○	○

[0154] (Note)
(A) HDPE Idemitsu petrochemical company make High density polyethylene Grade name: 440M
(B) LLDPE Dow Chemical Co. make, ethylene / octene 1 copolymer Grade name : as an FM1570
(C) IPP catalyst Isotactic polypropylene [limiting viscosity eta] =2.76 deciliter/g manufactured according to homopolymerization of a propylene in the heptane solvent using rac-dimethyl silylene (2-methyl-4-phenyl-indenyl) zirconium dichloride / MAO catalyst, An isopropylidene (cyclopentadienyl) (fluorenyl) dichloro zirconium / MAO catalyst is used as a (D) SPP catalyst [mmmm] =96.3%. By the toluene solvent system according to homopolymerization of a propylene Manufactured syndiotactic polypropylene [limiting viscosity eta] =0.89 deciliter/g, Cp* TiCl(tBuN (SiMe2))2 / MAO (the so-called CGC system catalyst) is used as a [rrrr] =86.5%(E) APP catalyst. By the toluene solvent system according to homopolymerization of a propylene As a manufactured atactic polypropylene [limiting viscosity eta] = 3.10-deciliter [/g] (F) LiPP catalyst Low isotactic polypropylene [limiting viscosity eta] =2.1 deciliter/g manufactured by the heptane solvent system using zirconium dichloride/MAO, (1, 2'-dimethyl silylene) (3-trimethylsilyl methylene-indenyl) (2, 1'-dimethyl silylene) [mmmm] =44.2%

[Translation done.]